

Remarks

This Amendment responds to the Office Action dated February 27, 2003. In the Office Action, the examiner objected to claims 7 and 8 due to an informality regarding recitation of a Markush group. Claims 7 and 8 have been amended to refer to "the group consisting of" as requested by the patent examiner.

In the Office Action, the examiner rejected claim 6 under 35 U.S.C. §112, second paragraph as being indefinite, particularly relating to the word "composite." Claim 6 has been amended to delete that word such that the claim now provides "dyeing the laminated fabric of said knit layer, aluminum sheet layer and non-woven fabric layer with a background color." Accordingly, applicant has overcome the indefinite use of "composite" and respectfully requests that the examiner withdraw this rejection of claim 6.

In the Office Action, the examiner rejected as being non-patentable claim 1 under 35 U.S.C. §102(b) in view of U.S. Patent No. 5,149,582 to LaMarca (herein "LaMarca '582"). The examiner rejected claims 2-5 and 10-11 under 35 U.S.C. §103(a) in view of U.S. Patent No. 4,901,738 to Brink (herein "Brink '738"). The examiner rejected claim 6 under Section 103(a) as being unpatentable over LaMarca '582; Brink '738 and U.S. Patent No. 5,568,666 to Seibert. The examiner rejected claims 7-9 and 12 under 35 U.S.C. §103(a) as being unpatentable in view of LaMarca '582; Brink '738 and U.S. Patent No. 3,094,547 to Heine ("Heine '547").

Further, the examiner rejected under the doctrine of obviousness-type double patenting claims 1-12 as being unpatentable over claims 1-12 and 19-21 of co-pending application by applicant Principle, Serial No. 09/872,942. Applicant respectfully submits that she will file a Terminal

Disclaimer thereby avoiding the obviousness-type double patenting rejection upon allowance of claims in both of these patents applications.

Applicant has amended claim 1 to recite "A cigar and cigarette burn resistant gaming table cloth which resists decomposition by burn and char formation by a lit cigarette or cigar for at least three minutes during direct contact exposure to the lit end of the cigar or cigarette." Further, claim 1 has been amended to provide "said aluminum acting as a heat sink and preventing decomposition by burn and char formation on the fabric for at least three minutes."

Support for these concepts is found throughout the patent specification. Particularly in paragraph 3, "Casino patrons dislike the look of stained gaming table covers (originating from spilled drinks) and table covers with burn marks are similarly unsightly. Patrons will avoid these stained and abused gaming tables ... the distressed look of the table engenders a poor quality image in the minds of casino patrons." "Hence, there is a need for a water resistant cigar and cigarette burn resistant gaming table of billiard table cover." Paragraph 5.

In other words, applicant seeks protection for a cigarette burn resistant cloth that prevents decomposition by burn and prevents char formation due to direct contact exposure to a lit cigarette for at least three minutes.

It is respectfully submitted that the references cited by the examiner are primarily concerned with flame resistant or flame retardant fabrics whereas the presently claimed invention is more concerned with a burn resistant fabric which has been more specifically identified as "preventing decomposition by burn and char formation on the fabric for at least three minutes." In Paragraph 13, it is an object of the invention to provide "a cigar and cigarette burn resistant gaming table cloth." In Paragraph 15, the gaming table cloth "significantly resists burning by a lit cigarette or a lit cigar

for about three minutes or more during direct contact exposure to the lit end of the cigar or cigarette." Paragraph 22 discusses experiments indicating that prior art gaming table covers burn in 11-20 seconds upon direct contact with lit cigarette or lit cigar which have an approximate temperature of 1200°F. "The cloth composite of the present invention does not burn unless the hot spot exposure exceeds at least 3 minutes of direct contact with a lit cigarette or lit cigar. It is believed that the aluminum acts as a heat sink and prevents burn on the fabric for up to 3-4 minutes."

In view of these explicit statements in the patent specification, the present invention is not primarily concerned with flame retardant fabrics but rather is concerned with burn resistant fabrics wherein burn resistant is further defined as "preventing decomposition by burn and char formation on the fabric for at least three minutes." The entire purpose of the new fabric was to avoid burn marks due to cigars and cigarettes on gaming and billiard table cloth. See Paragraph 3 (casino patrons dislike ... table covers with burn marks); Paragraph 5 (there is a need for water resistant cigar and cigarette burn resistant gaming table); Paragraph 13 (same); Paragraph 15 (a cloth which significantly resists burning by a lit cigarette or a lit cigar for about three minutes); and Paragraph 22 (the present cloth invention does not burn unless the hot spot exposure from the lit cigarette or lit cigar exceeds at least three minutes of direct contact). Hence, the present invention is not directed to a flame retardant or flame resistant fabric but rather is directed to a fabric which prevents decomposition by burn and char formation (such burn or char formation representing burn marks on casino table cloth and billiard cloth per Paragraph 3).

Persons with ordinary skill in the art of burn resistant and flame retardant fabrics recognize the relationship between flame retardant features and char formation. Exhibit A attached provides a glossary for the Flame Retardants Center which glossary separately identifies char (carbonaceous

residue resulting from pyrolysis or incomplete combustion), separate from fire retardant and fire retardants. (pp. A-2, A-3). Further the book Fire Retardancy of Polymeric Materials, Ed. Arthur F. Grand and Charles A. Wilky, Pub. Marcel Dekker, Inc. (2000) pp. 172-174, (Exhibit B attached) discusses the role of char in the study of thermal degradation in fabrics. p. B-3. In Exhibit C attached, persons of ordinary skill in the art recognize that the phrase "fire retardant" encompasses many factors including ease of ignition, flame spread, fire endurance, rate of heat release, ease of extinction, smoke evolution and toxic gas evolution. Exhibit D enclosed also discusses char formation and the relationship of char formation regarding flame retardant polymers. Exhibit E attached is a book Flammability of Fabrics, Charles Hilado, Technomic Pub. Co., Westport, CT (1974) pp. 11-24 and 59, 62 and 63, which discusses char life at p. E-4 and the production of char at p. E-5 and states that many flame retardants have a tendency to produce more char at pp. E-7 and E-8. The article "Flammability Measurements and Thermal Decomposition of Textiles" by J.E. Hendrix, et. al. and that same textbook Flammability of Fabrics, at p. E-11 graphically illustrates at p. E-12 that fabrics that produce more char have lower combustion temperatures as compared with fabrics that are not treated with flame retardant chemicals.

In other words, (a) production of char is a recognized characteristic in the flame retardant industry, that is, recognized by the person of ordinary skill in the art, and (b) typically char formation would be increased in flame retardant fabrics rather than prevented or reduced as claimed in the present invention. Further, the present invention is interested in preventing both burn and char formation for at least three minutes after direct contact exposure to a lit end of a cigar or cigarette. These attached references, and the fire retardant prior art references cited by the examiner, teach

away from the claimed invention which prevents decomposition by burn and prevents char formation on fabric for three minutes due to the direct contact exposure to the lit end of a cigarette.

None of the references cited by the examiner discuss preventing decomposition by burn and char formation on the fabric due to direct contact with a lit cigarette or cigar for at least three minutes as presently claimed in the present invention. The patent specification, and now the amended claims, are all directed to preventing decomposition by burn and decomposition by char formation. The articles attached hereto indicate that char formation is one of many physical characteristics which have an impact on the flame retardant feature of fabrics. However, the technology, at least as explained in Exhibits D and E indicates that fabrics which generate greater char have greater flame retardant characteristics. In the present invention, char formation and burn decomposition is avoided (because casino patrons dislike table covers with burn marks, Paragraph 3). Any resulting flame retardant characteristic of the gaming table cloth is, in the present patent application, irrelevant to the structure and the operation of the structure upon "direct contact exposure to a lit end of the cigar or cigarette."

LaMarca '582 is specifically directed to a flame barrier, puncture resistant fabric sheet as stated in its title. Flammability requirements are identified at column 1, line 25-30 and lines 35-49. LaMarca '582 specifically states that these flame tests involve a horizontal type flame test and a vertical type burn test and that "flame must be prevented from penetrating through the upholstery fabric." Col. 1, line 36. LaMarca '582 discusses a flame barrier composite sheet material at col. 1, line 66 and col. 2, line 3. In discussing the aluminum foil layer at col. 4, line 36, LaMarca '582 states "The metal foil provides a flame barrier and also serves as a heat sink in the resulting composite fabric cheap material and aids in stopping vertical flame propagation." Lines 40-43.

Further, at col. 5, lines 24-30, it is explained "It is recognized that the composite fabric sheet material of the [LaMarca '582] invention will have applications in a wide variety of fields where a highly flame and puncture resistant fabric sheet material is desired." In explaining the preferred embodiment of his invention, LaMarca '582 discusses the flammability specifications and fire block test at col. 7, lines 4-6. LaMarca '582 does not discuss preventing decomposition by burn nor decomposition by char formation.

With respect to Brink '738, that patent disclosure discusses a laser shield which claims are particularly directed to a laser resistant surgical drape. The laser shield claim format in Brink '738 is a similar claim format in that the present claim relates to a gaming table cloth which resists decomposition by burn and char formation by a lit cigarette or cigar for at least three minutes. The structural aspect of preventing both (i) decomposition by burn and (ii) preventing char formation for at least three minutes is explicitly recited in claim 1 of the present invention. In other words, the flame resistant fabric identified in LaMarca '582 is directed to a different composite cloth structure as compared with the presently claimed invention which is directed to a gaming table cloth which resists unsightly burn marks caused by a lit cigar or cigarette. Brink '738 discusses a need for a laser resistant surgical drape at col. 1, line 16 and line 59, col. 2, lines 16 and 48. More particularly, the laser shield in Brink 738 includes thermal plastic fibers which resist flaming when subjected to a carbon dioxide laser. Col. 4, lines 17-22. More significantly the laser shield in Brink '738 uses aluminum or many other metal foils such as copper, gold, iron, and steel. Col. 4, lines 40-50. In the present invention, other metal foils or sheets have been found to be unacceptable for the burn resistant fabric. Paragraph 48 (steel does not adhere to cloth layers and is too heavy).

Brink '738 also discusses a national fire standard which relates to ignition in 15 seconds or 20 seconds. Col. 7, lines 17-25. In direct contrast, the presently claimed invention resists decomposition by burn and resists decomposition by char formation for at least three minutes due to direct contact exposure to the lit end of a cigar or cigarette. The claimed invention describes a different structure for a different purpose which, most importantly, operates in a different manner when subjected to "direct contact exposure." The claimed prevention of char (and the resulting burn marks, Paragraphs 3, 13, 15 and 22) is not disclosed by the prior art. In fact, the prior art Exhibits D and E attached show that greater char formation enhances fire retardant features of a fabric.

Scibert '666 and Heine '547 do not show, teach or suggest a laminated fabric with an aluminum sheet which prevents decomposition by burn and char formation on a fabric for at least three minutes during direct contact exposure to lit end of a cigar or cigarette.

Accordingly, it is respectfully requested that the examiner withdraw the rejection applied against claims 1-12 and allow those claims in the present case.

Respectfully submitted,

Fleit, Kain, Gibbons, Gutman & Bongini, P.L.

June 17, 2003

By

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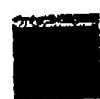
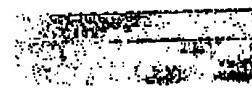
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Glossary

This glossary is partially inspired from the ISO 13943: 2000 -fire safety - vocabulary-

A - E F G - N O - T**after flame**

A flame which persists after the ignition source has been removed.

after flame time (s)

Length of time for which an after flame persists under specified conditions.

afterglow

Persistence of glowing after cessation of flaming or if no flaming occurs, after the ignition source have been removed

afterglow time (s)

The length of time for which an afterglow persists under specified test conditions.

arc resistance

The ability of a material to resist the influence of an electric arc along its surface, under specified test conditions

burned area (m^2)

That part of the damaged area of a material that has been destroyed by combustion or pyrolysis, under specified conditions. (See also damaged area - N 27)

burned length (m)

The maximum length of a material that has been destroyed by combustion or pyrolysis under specified conditions.

burning behaviour

All the physical and/or chemical changes that take place when an item is exposed to a specified ignition source.

calorific value (J/kg)

Heat produced by combustion of unit mass of a given substance.

• gross calorific value (J/kg)

<http://www.specialchem4polymers.com/IC/Flame-Retardants/index.aspx?id=3524>

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*Exhibit A**A-1*

The calorific value of a substance when the combustion is complete and any produced water is entirely condensed under specified conditions.

- **net calorific value ; heat of combustion (J/kg)**

The calorific value of a substance when the combustion is complete and any produced water is in the vapour state under specified conditions.

char (noun)

Carbonaceous residue resulting from pyrolysis or incomplete combustion.

combustible (adj.)

Capable of being combustible.

combustion

Exothermic reaction of a combustible substance with an oxidizer.

deflagration

A combustion wave, accompanied by an explosion, propagating at subsonic velocity.

detonation

A combustion wave, accompanied by an explosion, propagating at supersonic velocity and characterized by a shock wave.

end use conditions

The intended conditions to which an item will be subjected during its normal working life, when used in accordance with the manufacturer's instructions.

explosion

An abrupt expansion of gas which may result from a rapid oxidation or decomposition reaction, with or without an increase in temperature.

exposure time (s)

The length of time for which people, animals or items are exposed under specified test conditions.

A-Z E G-N Q-T

fire

Self supporting combustion spreading uncontrolled in time and space characterized by the emission of heat and effluent often accompanied by flame and/or glowing.

fire barrier (function)

The ability of a separating element to resist the passage of flame and/or heat and/or effluents.

fire barrier (product)

A separating element able to function as a fire barrier (function), for a period of time under specified conditions.

fire behaviour

The change in the physical and/or chemical properties of an item and/or structure exposed fire.

fire compartment

An enclosed space, which may be subdivided, bounded by elements of

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construction having a specified fire resistance.

fire effluent

The totality of gases, and/or aerosols (including suspended particles) created by combustion or pyrolysis.

fire exposure

The extent to which persons, animals or items are subjected to the conditions created by fire.

fire gases

The gaseous part of the products of combustion.

fire hazard

The potential for injury and/or damage from fire.

fire performance

The response of an item when exposed to a specific fire.

fire resistance

The ability of an item to fulfil for a stated period of time the required stability and/or integrity and/or thermal insulation and/or other expected duty specified in a standard fire-resistance test.

fire retardant (noun)

A substance added or a treatment applied to a material in order to delay ignition or to reduce the rate of combustion.

fire scenario

A detailed description of conditions, including environmental, of one or more stages from before ignition to after completion of combustion in an actual fire at a specific location or in a real scale simulation.

fire simulation

Mathematical representation of one or more of different interconnected phenomena governing a fire development.

flame

Zone of combustion in the gaseous phase usually with emission of light.

flame front

The boundary of flaming combustion at the surface of a material or propagating through a gaseous mixture.

flame retardance

The property of a material whereby flaming combustion is slowed, terminated or prevented.

flame retardant (noun)

A substance added, or a treatment applied to a material in order to suppress or delay the appearance of a flame and/or reduce its propagation (spread) rate.

flame retardant treatment

A process whereby improved flame retardance is imparted to a material or product.

flame spread

Propagation of a flame front.

flame spread rate (m/s)
Distance travelled by a flame front during its propagation, divided by the time of travel, under specified conditions.

flammability
The ability of a material or product to burn with a flame under specified conditions.

flammable
Capable of flaming under specified conditions.

flash-over
The transition to a state of total surface involvement in a fire of combustible materials within an enclosure.

fully developed fire
The state of total involvement of combustible materials in a fire.

A-E E G-N Q-T

gasification
Transformation of a solid and/or liquid material to a gaseous state.

glowing combustion
Combustion of a material in the solid phase without flame but with emission of light from the combustion zone.

gross calorific value (J/kg)
The calorific value of a substance when the combustion is complete and any produced water is entirely condensed under specified conditions.

heat flux (kW/m²)
The amount of thermal energy emitted, transmitted or received per unit area and unit time.

heat release (J)
The calorific energy which is released by the combustion of an item under specified conditions.

heat release rate : rate of heat release (W/m² or W)
The calorific energy released per unit time by an item during combustion under specified conditions.

heat stress
Conditions caused by exposure to elevated/reduced temperature, radiant heat flux, or combination of these factors.

ignitability
Measure of the ease with which an item can be ignited, under specified conditions.

ignition
Initiation of combustion.

ignition source
A source of energy that initiates combustion.

incandescence

Emission of light produced by a material when intensely heated. It can be produced by materials in a

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integrity
The integrity of a separating element when exposed to fire on one side, to prevent the passage of flames and hot gases or the occurrence of flame on the unexposed side, for a stated period of time in a standard fire resistance test.

intermediate scale test
Test performed on an item of medium dimensions.

L.C.50 : lethal concentration 50, (g/m³)
The concentration of toxic gas or fire effluent statistically calculated from concentration-response data to produce lethality in 50 % of test animals of given species under specified conditions.

large scale test
Test, which cannot be carried out in typical laboratory chamber, performed on an item of large dimensions.

limit oxygen index (LOI) (%)
The minimum concentration of oxygen in a mixture of oxygen and nitrogen that will just support flaming combustion of a material under specified conditions.

melting behaviour
The phenomena accompanying the softening of a material under the influence of heat (including deforming and dripping, but not flaming).

molten drips (noun)
Falling droplets of material which have been softened or liquefied by heat.

net calorific value : heat of combustion (J/kg)
The calorific value of a substance when the combustion is complete and any produced water is in the vapour state under specified conditions.

non-combustible
Not capable of undergoing combustion under specified conditions.

non-flammable
Not capable of burning with a flame under specified conditions.

A-E E G-N Q-T

opacity of smoke (dimensionless)
A measure of the attenuation of a light beam passing through smoke expressed as the ratio (N/T) of incident luminous flux (I_i) to transmitted-luminous flux (T) through smoke under specified conditions.

optical density of smoke
A measure of the attenuation of a light beam passing through smoke expressed as the common logarithm (i.e. logarithm to the base 10) [lg(N/T)] of the opacity of smoke.

pilot-light ignition
Ignition of combustible gases or vapours by a secondary source of energy, i.e. by for example, a flame, spark, electrical arc or glowing wire.

products of combustion
The solid, liquid and gaseous materials resulting from combustion.

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pyrolysis

The part of the irreversible chemical decomposition caused solely by a rise in temperature.

reaction to fire

The response of a material in contributing by its own decomposition to a fire to which it is exposed, under specified conditions.

real scale test

Test which simulates a given application, taking into account the real scale, the real way of working or installation and the environment.

screening test

A preliminary test used for ascertaining whether an item is likely to exhibit (or not) certain characteristics according to a standardized test method.

self-extinguishing

Deprecated term.

small scale test

A test performed on an item of small dimensions.

smoke

Visible part of fire effluent.

smoke obscuration

The reduction, (usually expressed as a percentage), in the intensity of light due to its passage through smoke.

smouldering

The combustion of a material without flame and without light being visible.

soot

Particulate matter produced and deposited during or after combustion.

specific optical density of smoke (dimensionless)

A measure of the opacity of the smoke produced by a specimen taking into account the optical density and factors characteristic of the specified test method.

surface spread of flame

The propagation of flame away from the source of ignition across the surface of a liquid or a solid.

sustained flaming

Persistence of flame on or over a surface for a minimum period of time.

thermal degradation

A process whereby the action of heat or elevated temperature on an item causes a loss of some properties e.g physical, mechanical or electrical.

toxic hazard

The potential for injury or loss of life by exposure to toxicants with respect to their potency, quantity, concentration and duration of exposure.

toxic potency

A measure of the amount of toxicant required to elicit a specific toxic effect.

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Transmittance (through smoke)

The ratio of transmitted luminous flux (T) through smoke to incident luminous flux (I) under specified conditions.

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Fire Retardancy of Polymeric Materials

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Exhibit B

B-1

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ISBN 0-8247-3379-6

This book is printed on acid-free paper.

Headquarters
Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution
Marcel Dekker AG
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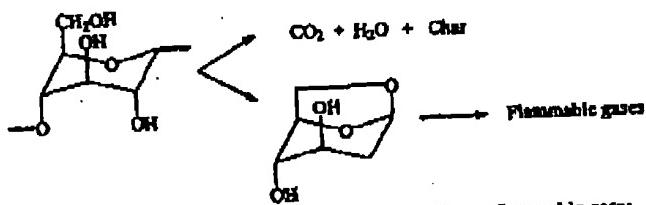
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Levchik and Wilkie

I. THE ROLE OF CHAR IN THERMAL DEGRADATION: FIRE RETARDANCY

Char, which is formed in the process of thermal degradation, can play several roles in fire retardancy. The formation of char in and of itself has a significant effect on the degradation because char formation must occur at the expense of other reactions that may form volatiles; thus, char formation may limit the amount of fuel available. An example of this occurs in cellulose, which may degrade either by a series of dehydration reactions that yield water, carbon dioxide, and char, or by a process in which levoglucosan is produced, which eventually leads to the formation of volatiles (1); this is shown as Scheme 1.



Scheme 1 Thermal degradation of cellulose to char or flammable gases.

The second role that must be considered is that once char is formed, it can influence further degradation. When an adherent and insulating layer of char is built up on the surface of a polymer, this layer may insulate the underlying polymer from the flame and, thus, make further degradation more difficult. This assumes that the combustion of char is a difficult process and there will be some dependence on the composition of the char layer. The typical char layer consists of an amorphous carbon along the way to graphitization; the extent of graphitization will influence the combustibility of the char layer. Enhanced thermal stability may result if the char layer contains an inorganic component in addition to carbon.

II. CORRELATION BETWEEN CROSS-LINKING AND CHAR FORMATION

A cursory review of the literature would lead one to believe that any cross-linked polymer will be inherently less burnable than a non-cross-linked polymer (2). In fact, this is not the case. The resistance to combustion of a polymer is in some way connected to both the number of cross-links and to the strength of the bonds that make up the cross-linked structure (3). In recent work from these laboratories, it

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Char Formation

has been observed that cross-linked methyl methacrylates, copolymers prepared by the radical polymerization of various dimethacrylates with methyl methacrylate, degrade at essentially the same temperature as does the homopolymer poly(methyl methacrylate). The most likely explanation is that the cross-linked structure is produced by very weak bonds that may be relatively easily cleaved thermally. Upon heating, the cross-linked structure is lost and the resulting polymer is now no different from that of methyl methacrylate and its degradation proceeds in the same way (4).

III. FORMATION OF CHAR

It is believed that the temperature at the surface of a burning polymer is close to the temperature at which extensive thermal degradation occurs (usually 300–600°C). The bottom layer of char, near the polymer surface, is at the same temperature, whereas the upper surface, exposed to the flame, can be as hot as 1500°C (5). Therefore, fire-retardancy chemistry is concerned with chars, which may be produced at temperatures between 300 and 1500°C.

A polymer passes through several steps in the formation of char. These include (a) cross-linking, (b) aromatization, (c) fusion of aromatics, (d) turbostratic char formation, and (e) graphitization. Turbostratic char refers to an incomplete process of graphitization when solid spheroids (precursors of graphite) appear in the molten carbonaceous material, typically at 500–700°C (6). At this point, the graphite layers are arranged in a parallel fashion, yet they are random in translation and rotation. The char formed during the combustion of polymeric materials is similar to the turbostratic char.

In fire-retardant terminology, all polymers are usually classified as non-charable or charable, depending on whether or not they produce char under pyrolytic conditions (5). In terms of the chemical processes governing thermal degradation, polymers may be divided into three classes (7,8): (a) polymers that undergo chain scission and volatilize with, at most, a negligible amount of the char formation [e.g., polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA)]; (b) polymers that undergo chain stripping reactions, producing unsaturation in the main chain with loss of hydrogen atoms and the pendant groups and give a moderate amount of char [e.g., poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN)]; (c) polymers that contain aromatic rings that can cross-link simultaneously with chain scission reactions and produce moderate to high amounts of char [e.g., aromatic polyamides (PA), polyesters (PS), polycarbonates (PC); polyimides (PI)]. Different authors may categorize each polymer in one or another category, depending on the emphasis they wish to place on a particular reaction.

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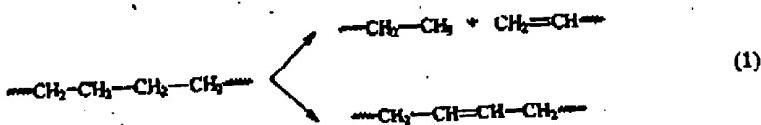
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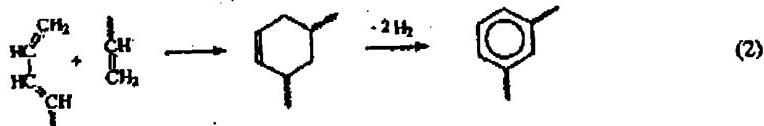
Levchuk and Wilde

A: Polymers That Naturally Produce Char

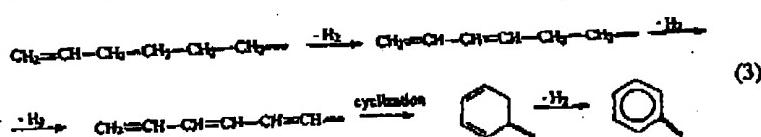
Under certain experimental conditions, even aliphatic polyhydrocarbons can produce some char. The dissociation energy of C—C bonds in hydrocarbons is 65–90 kcal/mol, depending on the structure, whereas C—H bonds have a dissociation energy in the range 90–105 kcal/mol (9). Because these energies are similar, dehydrogenation may compete with the chain scission at high temperature (10), as shown Eq. (1):



Vinyl chain ends activate hydrogen in allylic positions; the dissociation energy of the allylic C—H is ~ 85 kcal/mol (5,9) and this leads to dehydrogenation and formation of conjugated dienes. The dienes may react with an activated double bond (dienophilic reagent) and lead to aromatization, as shown in Eq. (2):



The diene may also undergo further dehydrogenation leading to a triene that may cyclize [Eq. (3)]:



This is a phenomenological model of carbonization of polyhydrocarbons. However, under the normal degradation conditions in an inert atmosphere, the formation of char by these processes is quite limited. One of the goals of fire retardant science is to promote these char-forming mechanisms.

Polyacrylonitrile (PAN) has been studied very extensively (11) as a potential source for the production of carbon fibers. It was shown (11-13) that the thermal degradation process of PAN strongly depends on heating rate. Under rapid

B-5

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Changing Nature of Fire Retardancy in Polymers

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ment of metals by plastics. It is not the cost of a material that determines material selection in an application, but what the final cost is to perform a function. As polymer options expand, as processing becomes more sophisticated, higher engineered parts become more practical. One may thus find combustible organic polymers in functions where metals once predominated. That can lead to unanticipated hazards (5).

IV. WHAT DOES IT MEAN TO BE FIRE RETARDANT?

Fire retardancy or flame retardancy or "FR" can be very much in the eye of the beholder. Combustibility can depend as much on fire conditions as on polymer composition. Whether a material is an "FR" material is very much in the context of tests. Whereas designing laboratory tests to fully simulate real fire conditions is not possible, the increased use of tests which measure fundamental properties, then using those properties in mathematical models, is becoming increasingly successful and is the subject of discussions elsewhere in this volume. The behavior of materials in a fire can be described by several factors (6):

1. Ease of ignition—how readily a material ignites
2. Flame spread—how rapidly fire spreads across a surface
3. Fire endurance—how rapidly fire penetrates a wall or barrier
4. Rate of heat release—how much heat is released and how quickly
5. Ease of extinction—how rapidly or how easily the flame chemistry leads to extinction
6. Smoke evolution—amount, evolution rate, and composition of smoke released during stages of a fire
7. Toxic gas evolution—amount, evolution rate, and composition of gases released during stages of a fire

A multitude of flammability tests measuring one or more of these properties have been developed. There are more than 100 tests in the United States alone. Other countries use different tests and rating systems, often making comparisons difficult. A material acceptable in one country may be rejected in another. A polymer resin may thus be more ignition resistant than its parent or than another resin and thus be "ignition resistant" or "flame retardant," but still have insufficient fire performance in the context of the tests appropriate for the application. That can lead to conflicts and miscommunication among resin supplier, customer, and end user. For example, in a recent legal case, a rubber manufacturer sold an ignition-resistant resin (UL-94 V-0) into an application. The application had its own industry test, which had few test facilities. The application test was known only vaguely to the resin supplier. The customer bought the resin, although it was

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marginal, because the resin was substantially less expensive than the alternatives. Years later in a product wide process change, the resin manufacturer found it necessary to reformulate its rubber. It formulated a new V-O product which was even more clearly V-O than the previous product. That "new improved product" was shipped to the customer under the same product number. Parts using the new resin were made and shipped. Only later did final product testing show that the new resin did not pass the end-product test. This necessitated a part recall from across the country. Litigation resulted. Who knew what? Who should have communicated what to whom? When? What quality control testing was needed and when, which would have shown that final parts did not comply with specifications? "Fire retardant" is not an absolute. It has a context which must be understood by supplier, customer, and user alike. That context needs to be discussed and communicated clearly.

V. IS THE USE OF "FR" RESINS MEANINGFUL?

In 1988, the National Bureau of Standards reported on a fire hazard comparison of fire-retarded (FR) and non-fire-retarded plastics (7). Applications included a TV housing, a business machine housing, upholstered chairs, a cable array, and laminated circuit boards. In each case, a non-fire-retardant resin and a corresponding flame-retardant resin were used in the application. It was concluded that representative fire-retarded products showed significantly enhanced fire performance. They found the following:

1. The average available escape time was more than 15-fold greater for the FR products in room burn tests.
2. The amount of material consumed in tests of the FR products was less than half the loss in the non-FR tests.
3. Fire-retarded products, on average, gave one-quarter the heat release of non-FR products.
4. The total quantity of toxic gas, expressed as CO equivalents, released by the FR products was one-third that for the non-FR products.
5. The production of smoke was not significantly different in room fire tests between FR and non-FR products.

"The study shows, then, that the proper selection of fire retardants can improve fire and life safety" (7). It was noted that such a conclusion should not be automatically expected, but that test and evaluation of candidate systems is necessary to ensure fire performance enhancement in the final application. It was also noted that production of carbon monoxide was not accurately predicted in less than room-sized tests. Instruments like heat-release-rate calorimeters are overventilated versus some room test scenarios and thus substantially underpredict CO.

C-2

Chapter 8 Char Enhancing Approaches to Flame Retarding Polymers

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info on char

more info

ABSTRACT: Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants (FR) [1-3]. Our research efforts focus on reducing polymer flammability by promoting char formation. Our approach to char promotion is to investigate additives which enhance charring, and to gain a fundamental understanding of the additives' mechanism of char formation with the goal of optimizing their performance. Char formation reduces the amount of small, volatile polymer pyrolysis fragments, or fuel, available for burning in the gas phase; this in turn reduces the amount of heat released and fed back to the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates incident energy away from the polymer surface. The char must also function as a mass transport barrier, by physically delaying the volatilization of decomposition products and/or chemically reacting with decomposition products. The physical structure of the char is important in this role. Thick, spongy char appears to be more fire resistant than brittle, thin char [4]. This char-enhancing approach is most successful when the polymer chars rapidly and early in the burning process. To be useful, the charring process must occur at a temperature above the polymer processing temperature, but below the temperature where rapid gasification of the polymer to combustible fuel occurs. This chapter is an overview of several new char enhancing approaches to reducing the flammability of polymers.

8.1 Introduction

Current efforts in our laboratory focus on several different char enhancing, inorganic-additive systems. All of these systems entail the use of inorganic materials as additives to organic polymers, such as commodity polymers, engineering polymers, thermoplastics and thermosets†. Under a class of additives best described as metal

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†Guest researcher at NIST from the Russian Academy of Sciences, Moscow, Russia.

‡ Certain commercial equipment, instruments, materials, services or companies are identified in this chapter in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

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Chemistry and Technology of Polymer Additives. Chapter 8. 1999; Blackwell Science Inc., Malden, MA, Ak-Malaika, S.; Golovoy, A.; Wilkie, C. A., Editors, 135-150 pp., 1999.

Exhibit D
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FLAMMABILITY OF FABRICS

VOLUME NINE
FIRE AND FLAMMABILITY SERIES

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INTRODUCTION

One of the goals of the Journal of Fire and Flammability and its supplements is to guide their content that within five years a complete collection of issues will be the basic literature source in this field of technology. Combinations of journal articles in areas of specific interest thus become a valuable literature resource, an the Fire and Flammability series of books embodies this concept.

Fabrics were the first materials in our society to be the subject of recent fire safety concern, in large part because of the amounts and extensiveness with which it is present in everyday life. The Flammable Fabrics Act and its amendments expire the government's concern about the fire safety of fabrics.

It is a measure of the importance of fabric flammability, that twenty articles contain useful information on the flammability of fabrics, and fourteen of these articles express this focus in their titles. Much of this information is novel and unique in coverage and viewpoint, and all of it is presented in the context of a mission of helping to make this world safer for its people.

These twenty articles are presented in this volume, with the hope that it will indeed prove to be a valuable literature resource in this field of knowledge.

FLAMMABILITY OF FABRICS

VOLUME NINE
FIRE AND FLAMMABILITY SERIES

TECHNOMIC Publishing Co., Inc. 1974
265 W. State St., Westport, Conn. 06880

2003, 05-21 15:20 4625 P.03

Printed in U.S.A.
Library of Congress Card No. 73-22116
Standard Book No. 0-87702-133-0

Received from <954 768 0158> at 6/17/03 2:35:21 PM [Eastern Daylight Time]

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(Received June 17, 1972)

FLAMMABILITY AND FLAME RETARDANCY OF FABRICS: A REVIEW

ABSTRACT: Flammability and flame retardancy of the commonly used fabrics are critically reviewed with reference to the importance of research on fabric flame retardancy mechanism of flame propagation, measurement of fabric flammability, progress in the science and technology of flame retardation, theory of flame retardant and the mechanism of flame and glow retardants, and glow retardation by the currently known flame and glow retardants. Several concluding remarks have been made. There are 65 references.

INTRODUCTION

ALMOST ALL TEXTILE fibers are organic polymers, most of which decompose below 300°C., producing gaseous products; some of these are flammable and ignitable under favorable conditions. Consequently, fibers constitute fire hazards. Inflameable textiles causes perhaps about 20% of the total loss of life and property due to fire of all kinds [1]. Relevant statistical surveys have recently been reviewed [1-3]. It appears that, as estimated in the United States, 150,000-300,000 persons per year suffer burn injuries as a result of clothing ignition. A high percentage of the victims are young children. Because loss of life and property and severe suffering are often associated with burn injuries in which clothing materials play some role [4], the issue of fabric flammability has become an international concern as is evidenced by a meeting [4] having representatives from many countries of the world. The consensus was that the consumer should be protected and such protective measures can be seen in the development of legislation against the use of highly or dangerously flammable fabrics" in countries such as Canada, France, Germany, Great Britain, Japan, Switzerland and the United States. Some of this legislation have been summarized [1, 4, 5]. The concern of the consumer and the impact of legislation have shown the pressing need for flame retarded fabrics and fibers for such applications as apparel, interior furnishings, automobiles, carpets, air craft, to name a few. The textile trade and allied industries are becoming more involved in research and development to reduce or retard fabric flammability, as is evidenced in the increased production and sale of flame retardants during the last few years. To whom correspondences should be addressed.

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Flammability and Flame Retardance of Fabrics

Table 1. Flammability Characteristics of Fibers
(from Ref. 21)

Fiber	Ignition Temp. °C	Maximum Flame Temp. °C	Flammability
Cotton	400	860	Burns readily with char formation and afterglow.
Rayon	420	850	Burns readily with char formation and afterglow.
Acetate	475	960	Burns and melts ahead of flame.
Triacetate	560	885	Burns readily and melts ahead of flame.
Nylon 6	530	175	Melts, supports combustion with difficulty.
Nylon 66	532	—	Melts, does not readily support combustion.
Polyester	450	197	Burns readily with melting and smoke.
Acrylic	560	885	Burns readily with smoking and spattering.
Modacrylic	—	—	Melts, burns very slowly.
Polypropylene	570	839	Burns slowly.
PVC and Polyvinylidene chloride	—	—	Does not support combustion.
Wool	600	941	Supports combustion with difficulty.

M.A. Karsan and H.K. Rouette

in additional product of the process. Flaming combustion occurs through radical reactions, and the radicals are formed by the pyrolysis of the fabric. Glowing and oxidation of char (mainly carbon) by air to give carbon dioxide and some carbon monoxide.

Measurement of Fabric Flammability

The flammability of a fabric (untreated as well as treated) is usually measured in terms of ignitability and combustibility. Ignitability is a measure of the ease with which a fabric ignites while combustibility is related to the rate of flame travel across a fabric specimen under a given test procedure. A number of test methods have been developed for evaluating the flammability of untreated fabrics and the resistance of flame retarded fabrics [2, 12-15]. For untreated fabrics, the rate of ignition and the rate of burning, as measured by the AA TCC 33-1962 [16], are used to compare flammability. Tweedie et al. [17] using vertical p method reported results of rate-of-burning measurements on a wide variety of fabrics obtained from various practical sources.

In addition, the rate of flame travel along an ignited fabric specimen may also be used as a criterion for flammability and such measurements on a series of fabrics have been reported [9]. The flammability of thermoplastic fabrics is evaluated by the same methods. However, in order to prevent melt dripping of the fabric, the test specimen is given support either by the use of a tracking or by using of threads (usually glass fiber) along the specimen. Such arrangements have been found to give reasonably good results of flammability measurement on thermoplastic fabrics [18]. Additional characteristics such as ignition temperature of the flame temperature (temperature inside the flame produced by a burning fabric) are also measured for evaluation of fabric flammability. Ignition temperature, "the maximum flame temperature" and the flammability [19-22] of cotton fabrics are shown in Table 1. The maximum flame temperature of a fabric was found to depend on specimen dimension and on the concentration of oxygen surrounding the specimen [20]. For flame retarded fabrics, the flame resistance is evaluated in terms of afterflame (duration for which a specimen (flames after removal of the ignition source), char length (vertical length of the specimen charred) and afterglow (time of glowing). Usually a test specimen is ignited by the application of a definite flame for a definite length of time and the above criteria are measured. Prescribed conditions vary from method to method and also depend on the requirements of the country concerned. The AA TCC 34-1969 vertical char test method [16] has been widely used and has been recently modified to test both natural and synthetic fabrics; the flame application time has also been reduced from 3 sec to 1 sec [23]. Results obtained for flammability measurement by the test methods mentioned above have been critically discussed [12, 13]. It appears that fabrics may rank in different orders, even if the same property is purportedly measured. Suchacki [24] suggested an "Index of Merit" defined as the ratio

of the burning time to the charred length for comparing the flammability of fabrics but it has never been accepted and used for evaluation of flammability to any extent. In recent years, the Oxygen Index (OI) method has gained popularity for flame retardancy measurement of untreated and flame retarded fabrics. Originally developed by Fenimore and Martin [25], the OI is defined as the minimum volume fraction of oxygen in a slowly rising oxygen-nitrogen mixture that will sustain combustion of the polymer. Tesoro et al. [10] found that OI measures the flammability of fabrics as a function of chemical composition of the fiber. The OI values of some of the fabrics as measured by Tesoro et al. are shown in Table 2. Willard [26] found that the oxygen index is a simple function of the added nitrogen and phosphorus content of the fabric. Miller et al. [27] studied the effects of various physical parameters e.g. fabric weight, specimen size, enclosure chimney, horizontal and vertical mounting and direction of gas flow on the OI and observed

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Flammability and Flare Retardance of Fabric

M.A. Karem and H.K. Rokette

few years [4]. The estimated market for flame retardant chemicals is expected to increase from 200 million pounds in 1971 to 850 million pounds in 1975 [6].

FLAMMABILITY CHARACTERISTICS OF FABRICS**Factors Affecting Fabric Flammability**

The flammability of fabrics is a complex phenomenon and is influenced by the characteristics of both the fiber and the fabric. The chemical composition of the fiber is the important fiber characteristic affecting flammability. In addition, chemical finishing operations such as mordanting during chrome dyeing of wool i.e. cross-linking [7], decrease flammability because the fragments resulting during decomposition are too large to be volatile. However, increasing molecular weight [7] decreases flammability because the fragments resulting during decomposition are too large to be volatile. However, increasing molecular weight of the fibrous polymer increases the decomposition temperature [8] and the weight of the decomposition reaction becomes more pronounced with exothermic nature of the decomposition reaction, weight per unit increasing molecular weight. Fabric properties such as construction, weight per unit area and surface smoothness affect flammability. Nielson and Richards [9] attempted to relate fabric flammability with the above properties, and found that regular fabrics burn more slowly than the lighter ones. For blends, the flammability is influenced by the nature and proportion of the constituting fibers; in particular by the so-called "scaffold" effect [4]. Tesoro et al. [10] found that the flammability of polyester increases with increase in the amount of cotton in the blend from 0 to 15% and remains virtually independent of the cotton content (up to 85%) in the blend. Moreover, the presence of "nonflammable fibers" in blends may reduce flammability of the flammable component of the blends, even to the self-extinguishing point. Tesoro and Rivlin [11] reported such a study on blends of Nomex with cotton and other flammable fibers, and they observed increased oxygen index values for the blends with increase in the percent Nomex in the blend.

Mechanism of Burning of Fabric

The mechanism of burning combustion in air is a complicated phenomenon but may be represented as shown in Figure 1. The process of ignition and burning of solid materials can be described schematically (Figure 2). If a flame attack the surface of a flammable material, the latter will ignite if a sufficient supply of oxygen is available. The heat produced during burning causes regression of the surrounding atmosphere and/or diffuses into the solid. During the regression of the surface, ablation of solid particles into the flame occurs, thus acting as fuel for the flame. Hence, the rate of surface regression depends on the direct oxygen attack and the ablation. The heat which diffuses into the solid causes pyrolysis, an endothermic process, and results in the formation of volatile products. The latter diffuse out to the surface of the solid and form additional fuel, which increases the flame temperature. In contrast to surface regression, pyrolysis forms a solid residue (char).

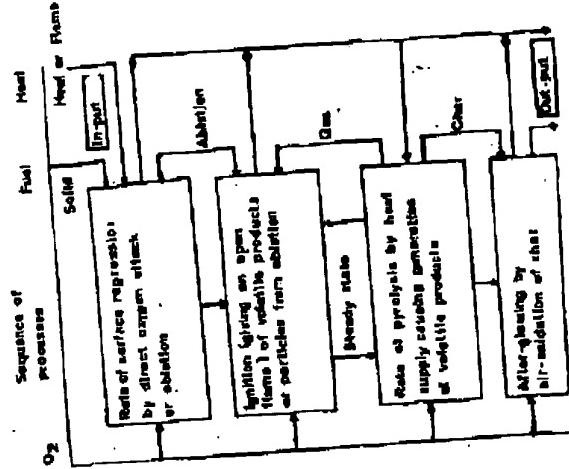


Figure 1. Flow of processes involved in burning of solid materials like fibers.

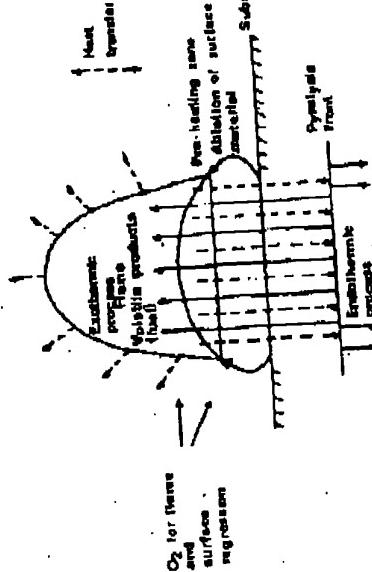


Figure 2. Schematic representation of the burning process of solids like fibers.

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Flammability and Flame Retardance of Fabrics

M.A. Karem and H.K. Rouellets

Table 2. Oxygen Index Values for Some Fabrics
(From Ref. 16)

Fabric - 100%	Fabric weight oz/yd ²	Oxygen Index
Aramid	6.5	0.182
Aramide triacetate	6.5	0.184
Acetate	6.5	0.186
Polypropylene	6.5	0.186
Vinylon (PVA)	6.5	0.197
Sevlon	6.5	0.197
Cotton	6.5	0.201
Nylon	6.5	0.201
Polyester	7.0	0.208
Wool	6.5	0.262
Dynel	4.8	0.282
Nomex N-4274	6.5	0.371
Phaxy (PyC) "95"		

that they affect OI significantly. DiPietro [28] studied the effect of pretreatment temperature of the IOT specimen on the OI of flame retarded cotton and found that the OI decreased with increasing temperature of the fabric. Hendrix and coworkers [29] studied the effect of moisture content on the oxygen index of cotton, polyester and their blends, both untreated and flame retarded, and found that a moisture content of less than 6% has very little effect. However, at a moisture content higher than 6%, the oxygen index values increase and this increase is more pronounced for flame retarded fabrics than for the untreated. The rapid increase in the OI technique is due to the precision with which the OI and intense interest in the OI technique of the results within a laboratory values can be measured and the reproducibility of the measurement by OI technique has been and among laboratories. Reproducibility of measurement by OI technique has been claimed to be 1-4% [30]. Recently, Miller et al. [31] developed apparatus and technique "A wheel-led flame apparatus" for the determination of flame propagation rate by moving fabric specimen at an appropriate velocity while maintaining the flame at a fixed position. It is claimed that data with a high degree of precision can be obtained by this method for both non-flusible and fusible fabrics, the latter without any support grid.

TECHNOLOGY OF FLAME RETARDANCYDevelopment of Flame Retardancy

Man's desire and need to reduce flammability of readily combustible materials go back to the prehistoric era, but attempts to impart flame resistance to fabrics are of relatively recent origin. In 1638 plaster of Paris was used as flame retardant for

canvas and in 1821 Gay-Lussac investigated a number of inorganic salts as flame retardant for textile fabrics. From then until about 1950, a limited amount of a hoc research was done. Research and development has been increasing at a fast rate during the past 10-20 years. The early work was concerned primarily with cellulose fabrics and has been reviewed from time to time [30-36]. Ramsey [37] has summarized patent literatures on flame retardant textiles. The introduction of synthetics and blends and their wools has necessitated the development of flame retardants for such fabrics. Some of the relevant literature have been reviewed [1-21]. Namez [21] provided a good survey of the techniques and flame retardants used to impart flame resistance to polyester, nylon, acrylics and a few other synthetic fibers. A large number of diverse compounds have been applied to fabrics, particularly to cotton. It appears that the majority of flame retardants contain phosphorus, nitrogen and halogen. In recent years some work has been done to explore potential of boron containing compounds as flame retardant to fabric [39, 40].

Techniques of Fabric Flame Retardation

Several different approaches have been used for flame-retarding fabrics. These are: finishing fabrics with flame-retarding chemicals, adding flame retardants to polymers before their ultimate extrusion, copolymerization and chemical modification of fiber. Chemical modification involves reaction of the polymer with some chemicals and the product is flame retardant. Examples include phosphorylation of cellulose and introduction of chlorine into polyester. In the copolymerization process one of the monomers contains a flame retardant element, e.g. chlorine, and is copolymerized with a second monomer so that the polymer contains its flame retardant in the chain. Of the four approaches, finishing appears to be most widely used in textile field. Flame retardants used for textile finishing may be put into two general classes, unreactive and reactive. Apparently such a classification is based on whether or not the flame retardant reacts with the fiber (polymer) at some stage during application of the retardant to fabric. The unreactive class includes a host of inorganic and organic compounds, most of which are salts. Water or organic solvent soluble compounds are applied from solution while the insoluble compounds are formed *in situ* on the fabric, e.g., WO_3 and SnCl_4 . The unreactive retardants are cheap, they are nondurable or semidurable to washing, depending on whether the retardant is soluble or insoluble in the washing solvent. Finishing includes THPC-polymers, APO and APO-THPC. Both APO and THPC are patent pending, and also cross-linking agents for cellulose. APO is capable of forming both homo and copolymer and such polymers have been formed on cotton to

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Supplying these compounds on cotton from water solution and curing at elevated temperature, THPC forms cross-linked polymers with a number of polyfunctional molecules, e.g., amines, ammonia, acids, phenols and APO. It appears that both APO and THPC in addition to forming polymer react with cellulose. Most of the work on these two compounds as flame retardants for cotton have been studied [41]. Recent interest has been focused on another derivative of THPC, tetrakis[*tert*-butylphosphonium] phosphonium [42]. Other reactive flame retardants for cotton include cyanamide-phosphonic acid [46], methylol dicyanamide, trimer of phosphonitrilic chloride (PCl_2)₃ [47]. Other reactive flame retardants for cotton include cyanamide-phosphonic acid [46], methylol dicyanamide, trimer of phosphonitrilic chloride (PCl_2)₃ [47]. The principles of flame retarding blends are basically the same as those of single components. However, it is usually necessary to flame retard all the components. Since flame retardants are specific in their effect, it may be necessary to use more than one type of flame retardant for blends. Some of the recent studies in this area have been reported by Kruse [4].

Synergism in Flame Retardancy

Incorporation of nitrogen or halogen (F, Cl and Br) into a phosphorus containing flame retardant has been found to increase the flame retarding efficiency. Examples include brominated phosphates, THPC-NH₃ polymer, and phosphonitrilic chloride. Similarly, certain mixtures of compounds have been found to be more efficient flame retardants than the constituent compounds. Examples include borak boric acid, organic phosphate-urea, arimony oxide-organic chloride, THPC-NH₃, THPC-diamine etc. [48]. Such increase in the flame retarding efficiency is an example of synergism and is an attractive field of research both from theoretical as well as practical view points.

MECHANISM OF FLAME RETARDANCY

General

The theoretical aspect of the mechanism of fabric flame retardancy is complicated both because of the complexity of the burning process itself, which varies from polymer to polymer, and because of the diverse nature of the compounds used as flame retardants. A generalized and consistent theory of flame retardancy applicable to all polymer is yet to be evolved, although much effort is being given in recent years to understand flame retardancy. It appears [49] that much of the present knowledge is speculative. However, cellulose has been widely studied and a wealth of information is available. Several theories based on this information, some

of which is empirical and intuitive, have been put forward, but a systematic study of the mechanism of flame retardancy in other polymers has begun only recently [49]. However, certain generalized statements pertaining to the nature of the flame retardants can be made.

1. Flame retardant effect of a compound is "catalytic," although a "high minimum" (10 percent add-on is required to obtain a "satisfactory" flame retardancy. This minimum add-on varies from polymer to polymer e.g. for cotton retardant viscose requires higher add-on than cotton.
2. The effectiveness in terms of add-on of flame retardants depends on many factors such as thermal stability of both retardant and the polymer and chemical reaction at elevated temperature of the flame retardant with the basic polymer [39].
3. Flame retardants are specific in their effect i.e. a compound may be a good flame retardant for cellulose but may not have any effect on polyester.
4. Organophosphorus compounds are especially effective for hydroxyl containing polymers e.g. cellulose, but their effectiveness does not appear to depend significantly on their structure. However, compounds decomposing above their flanking temperature (400°C) are ineffective.
5. The efficiency of halogen containing flame retardants increases in the order Cl, Br, I and halogens on aromatic structure are less effective than those on aliphatics [50, 51].

The Function of Some Flame Retardants

In principle flame retardancy can be achieved by affecting any or all of the stages of burning of polymer. These stages are (Figure 2) ignition, pyrolysis and flaming. Derivation of the function(s) of flame retardants is a formidable piece of work because of the many interacting variables involved in flame retardancy. Nevertheless, some generalizations concerning the function of flame retardants pertinent primarily to cellulose (but perhaps applicable to other polymers) can be made.

1. Phosphorus containing flame retardants act predominantly in the solid phase and affect pyrolysis of the polymer.
2. Halogen containing flame retardants act predominantly in the gas phase and affect the flaming reaction by acting as free radical scavengers; they may also affect the solid phase or in both phases.
3. Differential thermal analysis (DTA) shows that flame retardants lower the decomposition temperature of certain polymers [28, 39, 52-55].
4. Thermogravimetric analysis (TGA) shows that many flame retardants affect the weight loss of flame retardant fabric occurs at higher temperature compared to the untreated fabric [28, 63-65].

E-7 - 18 -

M.A. Kazem and H.K. Rouerie

Flammability and Flame Retardance of Fabrics

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5. Flame retardants may lower the heat of combustion of the polymer because less combustible gases are produced; this in turn affects pyrolysis of the polymer.
6. The non-combustible gases produced may reduce the exothermic surface regression because they dilute the oxygen necessary to attack the surface.
7. Flame retardants may form a coating film around the fiber such that oxygen necessary for flaming cannot attack the surface directly. Flame retardants may decompose, produce non-flammable gases which dilute the pyrolysis products to a concentration below that which is required to sustain flaming.
8. Flame retardants may act as inhibitors for the free radical flaming reaction e.g. halogens, acting as free radical scavengers in the flaming reaction.

Pyrolysis and Flame Retardancy

Pyrolysis of the polymer supplies fuel for flaming; hence it has been of utmost interest to study the effect of flame retardants on pyrolysis. With the exception of a few, the reported work is related to cellulose and an excellent review has been published [66] covering the basic aspects of cellulose pyrolysis which will not be discussed here. It appears that all work leads to a common conclusion that flame retardant cellulose, and probably most other fabrics, produces more char and less flammable gas. In addition, flame retardants catalyze the pyrolysis of a polymer [57, 58]. A recent mass spectrometric study [58] shows that the pyrolysis products from untreated cotton do not differ qualitatively from those of flame retarded cotton, although the proportion of the flammable gases in the latter is reduced. The effect of this increased or decreased availability of pyrolysis products reduced. The result is to create an imbalance in the fuel to oxidizer ratio in the flaming reaction. A combustible mixture will undergo flaming reaction only over a narrow range of fuel to oxidizer ratio, called the lower and upper flammability limits [59]. The flame becomes unstable and may extinguish, if the fuel is exhausted or if the chemical nature of interaction depends, among others, on the chemical stability. In the case of cellulose and phosphorus containing flame retardants, it is speculated that the phosphorus compounds are converted to phosphoric or polyphosphoric acid which acts as dehydration catalyst for cellulose [49].

Synergism in Flame Retardancy

Basal aspect of synergism is a relatively new field of investigation and hence very little progress has been achieved. Only a limited number of systems have been studied. It is felt that the mechanism of synergism is depicted primarily by the thermal reaction of the constituent compounds. For the P-N synergism, Hendrix [60, 61] has shown that some organic phosphate in the presence of urea forms phosphoramide and the latter acts as flame retardant for cellulose. The

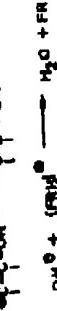
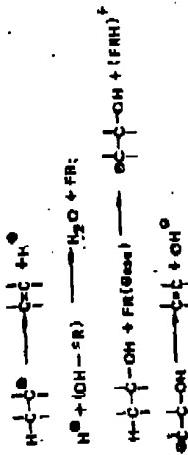
Dehydration Theory of Flame Retardancy

In principle a theory should be able to explain the mechanism of action of flame retardants and in addition, should be able to predict new retardants. Such a theory has yet to be evolved. However, several theories have put forward for cellulose. These are: the coating, the gas, the thermal and chemical theories and they have been described elsewhere [62]. The former appears to be more general and applicable to a large number of compounds that are applicable only to a limited number of flame retardants. The chemical theory was developed by Schuylen [63], it assumes that

The chemical theory was developed by Schuylen [63], it assumes that



FR = Flame Retardant



GLOW RETARDANCY

Glowing (flameless combustion) is due to the oxidation of carbon (the carbon dioxide). Thermolabile phosphorus and boron containing compound some metallic oxides have been found useful as glow retardants [64, 65]. Some postulations have been put forward to explain glow retardancy of cellulose. It is felt that the mechanism of synergism is depicted primarily by the oxidation of carbon to carbon monoxide is less exothermic than that to CO₂ and it has been proposed [66] that glow retardants divert oxidic dioxide and it has been proposed [66] that glow retardants divert oxidic

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carbon to the less exothermic carbon monoxide so that the heat of oxidation is insufficient to sustain further oxidation of carbon. In addition, it has been proposed that 'glove retardants' may coat the "active oxidation sites" in the char to prevent further oxidation. Furthermore, boron and phosphorus containing glove retardants were proposed to act as inhibitors for the oxidation of carbon by interfering with the electron transfer process in the oxidation of carbon [66].

CONCLUDING REMARKS

The need and importance for flame retardant fabrics are increasing at a faster rate than ever before. A large number of test methods are available for evaluating flammability of fabrics, but a method which can simulate the flammability being used in actual use is far from a reality, although efforts are continuously being made to approach this goal. Nevertheless the current test methods provide data which may be used to classify fabrics as slow or fast burning, flammable, less flammable or more flammable under specified conditions.

Very little is known about the basic aspects of flammability and flame retardation of fabrics other than cellulose which shares most of the literature in this field, and much is known about the basic and applied aspects of flammability and flame retardation of cellulose. Studies on synthetic fibers and their blends with natural fibers have been neglected in the past. In view of their increasing use, more efforts should be directed towards understanding basic aspects of flammability and flame retardation of synthetics and blends, and it appears that activity in this area is gaining momentum.

Although a large number of flame retardants are known particularly for cellulose fibers, only a very few of them possess any reasonable fastness to normal home laundering. In addition, most flame retardant finishes affect both the physical properties and the aesthetic values of fabrics. Only from the results of systematic studies, may it perhaps be possible to tailor flame retardants which would meet most, if not all the requirements asked for by the consumers.

Flammability and flame retardation of polymeric materials, particularly fabrics, is an interesting, challenging and fruitful field for investigation and it remains up to scientists to explore and develop this rather unsystematic and unorganized branch of science and technology.

ACKNOWLEDGMENTS

Thanks are due to the Sun Chemical Corporation (USA) for financial support and permission to publish this paper and to Prof. H. Zollinger for discussion.

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Fire Studies in Oxygen-Enriched Atmospheres

V. A. Dorf

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ABSTRACT

Studies of the effects of environmental parameters upon hyperbaric environments and evaluations of materials for flammability in oxygen-enriched atmospheres have been conducted. Burning rate data for a standard material in nitrogen and oxygen-helium mixtures are presented and a technique for measuring flammability in oxygen-enriched atmospheres is discussed. Tentative recommendations for fire resistance for materials are included.

INTRODUCTION

The ever-increasing application of oxygen-enriched atmospheres in hyperbaric chambers, oxygen tents and divers' decompression chambers has pointed up to the vital need for research into the combustibility of materials used in these environments. Although fires associated with the use of these environments are rare, they have occasionally occurred and often fatal results [6, 7, 8, 9]. In order to eliminate any one of the three fundamental prerequisites for combustion, namely, an ignition source, a fuel and an atmosphere capable of supporting combustion, it is often difficult or impossible to remove an ignition source, a fuel and an atmosphere simultaneously. Attempts should therefore be made to eliminate oxygen-enriched environments with absolute certainty. In practice, it is often difficult or impossible to remove all three essential factors. Requirements with respect to the above factors upon chamber should be minimized as much as possible.

In order to evaluate the contributing effects of the above factors upon chamber should be reduced to a minimum. A study has been conducted to determine the minimum oxygen concentration required for combustion of solid flammables in the presence of nitrogen at atmospheric pressure. The following conclusions were reached:

* An oxygen-enriched atmosphere (OEA) is generally defined as an atmosphere with more than 21 mole-% oxygen and/or contains a partial pressure of oxygen greater than 0.

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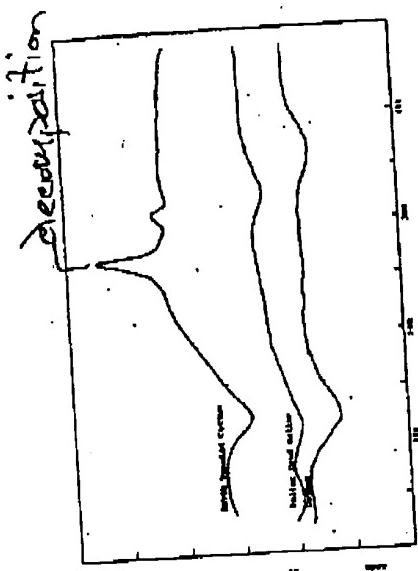


Figure 9. DTA comparing THPOH treated cotton and sulfur dyed cotton fabrics with bleached cotton in air at atmosphere using a 2 mm capillary tube, glass reference, and a 20°C/min heating rate starting at 25°C. Base line slope is +0.2 mV/min. Heating rate 5°C/min. ΔT is 0.5 mV/division.

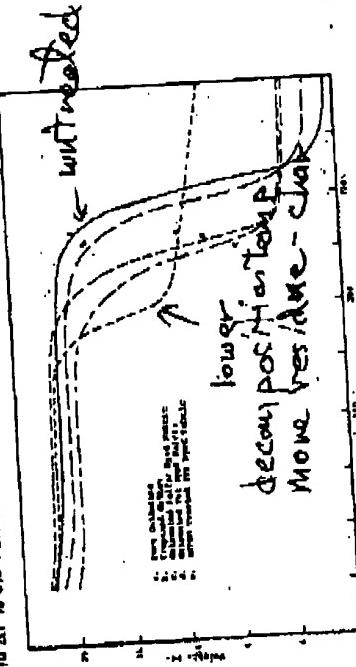


Figure 10. TGA of pure cellulose, prepared cotton fabric, sulfur dyed cotton fabric, vat dyed cotton fabric, and THPOH treated vat dyed fabric using 1% Kaurimine nitrogen atmosphere. Heating rate 5°C/min. Residue shift, 5% division vertical scale.

Fabric	T _d °C	% R	O.D.
Pure Cotton Cellulose	380	0.83	—
Prepared Cotton Fabric	385	9.18	20.27
Untreated Sulfur Dye Control	315	6.51	19.57
Untreated Vat Dye Control	320	12.80	21.17
THPOH Vat Dye (30%)	276	43.16	41.58

Table 3. Overall Decomposition Temperatures, Percent Residues and Oxygen Demand Data for Selected Cotton Fabrics.

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sent more quickly than the untreated fabric. While the total amount of volatile products may be lower with A, they are produced quickly with A because the finish catalyzes the decomposition of the fabric.

At both room temperature and at 400°C, will produce approximately 20% CO_2 , H_2O and nonburnable carbon and nonburnable inorganics. The burnable gases from B at 400°C are and 75% burnable gases. The burnable gases from A at the same temperature. This is ad more slowly than those from A at the same temperature. This is by the quicker ignition of A at 400°C. Clearly this result means that it is to be very careful when defining flame retardance. Some obvious which may influence flame retardance and make it difficult to measure

chemical composition of fabrics, dyes, finishes and blends. Each of factors changes a fabric's ease of burning and the temperature at which fabric flaming occurs. This may determine a fabric's ease of burning or destruction of the fabric. This may determine a fabric's ease of burning cause of accessibility of heat to the fiber surface or presence of a com-
mon adulterant is present in the fabric. The temperatures to which it is used. The final use of a fabric, that is, the temperatures to which it is subjected, will influence its flammability. This test indicates that no single test will effectively define a fabric's resistance to flaming. The results of any single test would be difficult to correlate to use.

TGA And Oxygen Demand

Thermal analysis techniques can determine decomposition temperatures of a given sample. Every cotton sample soldes during the combustion of a given sample. Every cotton sample is lowered led shows that the decomposition temperature of cotton is lowered. The adulterant may be a softener. An adulterant is present in the fabric. The adulterant may be a softener. If flame resistant finish or residues not removed during the preparation of samples. Differential Thermal Analysis (DTA) studies show that not only is the fabric differential important, but that the mode of decomposition of fabric is changed when resistance to flaming is achieved. Figure 9 illustrates the results obtained when three different cotton samples were studied. The lowest point of the 100% cotton endotherm is at 360°C, while the lowest point of the dyed cotton endotherm has been shifted to 320°C because of the effects of sulfur dye. However, the analysis indicates that these modes of decomposition remain essentially the same. On the other hand, the addition of products lowers the onset decom-
position temperature and that the percentage residue varies with residual temperature and that the percentage residue varies with residual temperature. A major residue of the sulfur dyed fabric is associated with a 160°C decomposition below that of pure cotton cellulose, even he addition of 65 degrees